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Carbon dioxide capture and bioenergy production using biological system – A review

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ABSTRACT

With the growing use of fossil fuels and industrial activity, the amount of carbon dioxide (CO_2) emission is continuously increasing and is considered a primary contributor to climate change. CO_2 emissions from stationary resources (coal fire, cement plants, and other industry) can be reduced by using various carbon capture and sequestration (CCS) technologies. In this article, recent advancements in various biological methods (i.e., carbonic anhydrase (CA), hydrogenation of CO_2 to formate, reduction of CO_2 to methane, CO_2 conversion into methanol by enzyme cascade, and the role of RuBisCo enzyme) that have been reported for CO_2 capture are discussed, along with their advantages and limitations. A brief overview of other physicochemical (absorption, adsorption, cryogenic, and membrane) technologies is also provided. Although biological methods are eco-friendly and can be performed under ambient conditions, these approaches are still not cost effective, as the reactions require cofactors, and the enzymes lose activity when exposed to hot flue gas and ionic liquids. Most captured CO_2 is stored by mineralization using a geological and ocean storage method without providing any economic benefit. It is a question of interest as to how we can utilize CO_2 and generate revenue. Utilization of CO_2 as a feedstock to produce bioenergy is a possible approach. Various microbes capable of utilizing CO_2 as feedstock and producing biofuels (biodiesel and bioalcohol) have been reported. These two technologies, i.e., CO_2 capture and bioconversion of CO_2 into bioenergy, can be integrated to develop a process that not only mitigates CO_2 effects on the environment but also solves energy problems while generating revenue.

1. Introduction

Carbon dioxide (CO_2) is produced naturally as well as by human activities [1]. Naturally, it is produced though the decomposition of organic material, respiration, or ocean release [2,3]. According to a report published in nature, CO_2 emissions from the soil and oceans have increased during the past few decades because of a temperature increase that triggers microbes to degrade organic material as well as other human activities (deforestation, burning of fossil fuels) [4–6]. The share of CO_2 produced by human activities is very low as compared to natural sources, but it disrupts the natural balance, as nature is able to remove nearly the same amount of CO_2 as is produced by natural sources [7]. CO_2 level is continuously increasing and have already reached a dangerous level. According to one estimate, 42.84% of CO_2 originates from the oceans, 28.56% from plants and animals respiration, 28.56% from decomposition, and 0.03% from volcanic eruptions [8]. CO_2 is considered a major greenhouse gas that results in climate change [9]. An increase in greenhouse gases has caused global warming resulting in the melting of polar ice, a rise in sea level, collapse of ecosystems, and severe climatic events (hurricanes, droughts, and floods) [10,11]. The Kyoto Protocol and Paris Agreement fixed goals and responsibilities for participating countries to reduce CO_2 emissions and limit a temperature increase to below 2 °C during this century [12,13]. Therefore, it is important to develop a range of technologies that can reduce CO_2 emissions and capture it from the atmosphere.

To reduce CO_2 levels, different approaches can be used, e.g., plant

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more trees, burn less coal, improve the efficiency of coal fire-based plants, and capture and store released CO_2 [14]. Plants are natural scavengers of CO_2 and convert it into biomass in the presence of sunlight through photosynthesis. Under the Kyoto Protocol, measures such as reduced deforestation and planting of trees have been introduced; however, it is difficult to protect young plants from drought, fire, and disease [12]. Other barriers are the availability of land as there is competition to grow more food crops. The approach of burning less coal seems difficult as coal is an abundantly available inexpensive source of energy and no other alternative is available. Researchers are working on improving the efficiency of coal-based plants but are only able to reduce CO_2 emission by 10–20% [14]. CO_2 capture and its transformation into other important products is a fascinating approach as it would aid in mitigating CO_2 release into the environment and allow continued use of coal to fulfill energy demands.

There are different means to capture CO_2, i.e., biological and physicochemical [15]. The main physicochemical routes used for CO_2 capture include absorption, adsorption, and cryogenic distillation [16–18]. These methods have their own advantages and disadvantages; however, this review article is more focused on biological methods of CO_2 capture as it is a clean and green approach (Table 1) [13]. Carbon capture and sequestration (CCS) technology using biological systems is an ecofriendly means to reduce atmospheric CO_2 and its emission from stationary sources (e.g., coal-fired plants and the cement and steel industries). Various microbes that can capture CO_2 such as *Acetabacterium woodii, Clostridium aceticum, Clostridium kluyveri, Clostridium ljungdahlii, Chlorella vulgaris, Rhodococcus erythropolis, Ralstonia eutropha, Synechococcus elongatus, Rhodobacter sphaeroides* have been reported [19–21]. Different mechanisms are involved in CO_2 capture, such as the hydration of CO_2 to bicarbonate by carbonic anhydrase, the reduction of CO_2 into methane, and the conversion of CO_2 to formate and methanol [22,23].

Energy demand is increasing every day to fulfill humanitarian and industrial requirements [24,25]. Liquid fuels (such as biodiesel and bioalcohol) are more appealing, as they have a higher energy density and can be readily stored and transported using existing infrastructure [26–28]. Integration of CO_2 capture and energy production technologies can be an alternate source of renewable energy that can help to mitigate CO_2 effects on the environment. Captured CO_2 can be used as a feedstock for microbial fermentation to produce bioenergy resources (biodiesel and bioalcohol) [29–31]. The main objective of this article is to discuss various possible biological approaches used for CO_2 capture and its utilization as feedstock for bioenergy production (Fig. 1).

2. Biological methods for CO_2 capture

Three types of strategies have been reported for CO_2 capture, i.e., pre-combustion, post-combustion, and oxy-combustion (Fig. 2) [14]. During the pre-combustion process, first coal is subjected to gasification to produce syngas (a mixture of gases containing carbon monoxide and H_2) after which syngas steam is applied to a waste-gas shift where CO reacts with water and produces CO_2 and H_2 [32]. The produced CO_2 can be captured using various available biological methods and the remaining H_2 is diluted with N_2 to run turbines. During the post-combustion process, CO_2 is captured from the flue gas once fuel is fully burned in the presence of air. Nitrogen is the main component of flue gas when coal is burned with air. The CO_2 capture process can be simplified if flue gas is free of nitrogen and it can be achieved by performing coal combustion under pure oxygen (> 95%) in a process termed oxy-combustion [33]. The main advantage of the oxy-combustion process is that the released flue gas is mainly composed of CO_2 (> 80%) and only a purification step is further needed [32]. The main disadvantage of the process is the requirement of pure oxygen which makes the process costly. Released CO_2 can be captured using various biological methods (Fig. 2).

Table 1
Comparison of biological and other physicochemical CO_2 capture technologies.

Category	Technology	Mechanism	Advantages	Disadvantages
Biological	Carbonic anhydrase (CA)	Catalyzes reversible conversion of CO_2 to bicarbonate.	It is a metalloenzyme and does not require other costly cofactors.	Flue gas is emitted at a higher temperature while CA can perform under mesophilic conditions. Ionic liquid is used to facilitate CO_2 capture and energy is required to regenerate ionic liquid and recover CO_2.
	Hydrogenation into formate	Formate dehydrogenase catalyzes hydrogenation of CO_2 to formate.	It is a single enzymatic reaction and easy to control. Formate can be directly used as feedstock for synthesis of other resources.	Requires *β*-nicotinamide adenine dinucleotide as a cofactor which affects the economics of the process.
	CO_2 conversion into methanol	A multistep cascade reaction catalyzed by formate dehydrogenase, formaldehyde dehydrogenase, and alcohol dehydrogenase.	Methanol is a type of fuel and directly used as an energy source.	Multienzymes reaction are difficult to control. All the enzymes need a cofactor which makes the process costly.
	Reduction into methane	Engineered nitrogenase able to reduce CO_2 into methane.	Methane can be directly used as an energy source.	There is no natural enzymatic system reported for CO_2 reduction into methane and the only means is to use engineered nitrogenase and microbial electrolysis cell.
	RuBisCo enzyme	Capture CO_2 by carboxylation of ribulose-1,5-bisphosphate.	Most plant and algal systems use this enzyme and directly integrate CO_2 via a glucose synthesis pathway.	RuBisCo is less specific towards CO_2 compared to O_2.
Physical	Adsorption	Activated carbon, zeolite, and meso-porous silica used to adsorb CO_2.	No use of chemicals and easily applied to post-combustion capture without any modification in plants.	Requires high pressure as the material is sensitive to high temperature and shows low selectivity.
	Membrane separation	Separation of CO_2 from flue gas occurs by passing through selective semipermeable membrane.	High mass transfer.	High operation cost because of easy membrane blockage. Requires high pressure and low moisture content.
	Cryogenic method	Works on condensation and cooling principle.	Can be directly converted into liquid CO_2 which is easy to transport.	Requires considerable energy for the condensation and cooling process.
Chemical	Chemical absorption	Mostly primary and secondary amines are used to convert CO_2 into carbonate and bicarbonate.	Easy to recover CO_2 from the solvent.	Techniques applicable only to flue gas of low concentration. Uses chemicals that are not ecofriendly.
	Mineralization	Reaction with other metal oxides forms stable carbonate.	Suitable for long-term storage of CO_2.	Requires a large amount of reagents and the process is not cost effective.

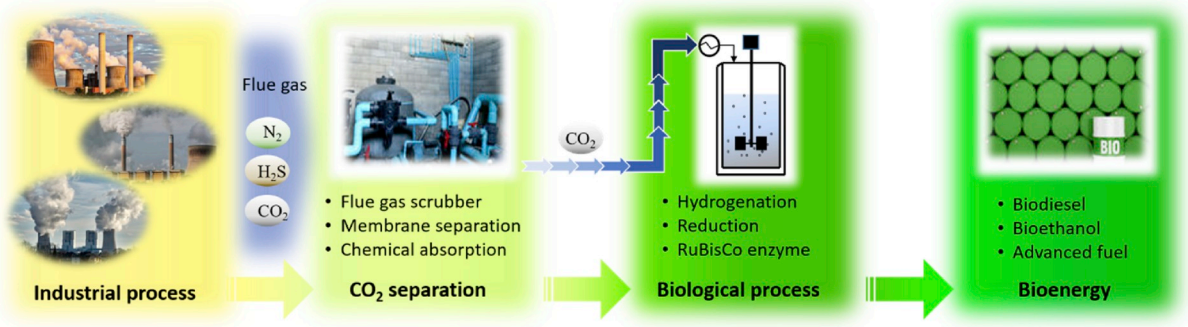

Fig. 1. Overall scheme for CO_2 capture and bioenergy production.

2.1. Carbonic-anhydrase-mediated hydration of CO_2 to biocarbonate

Carbonic anhydrase (CA) is found in all organisms as it plays a role in CO_2 metabolism [34]. CO_2 is able to freely diffuse in and out of the cell, while carbonate is poorly soluble in lipids and needs a transporter for its diffusion through the membrane [35]. CO_2 and HCO_3^- exist in equilibrium and their interconversion is catalyzed by zinc-dependent CA in which the conversion of bicarbonate into CO_2 facilitates transport into the cell while CO_2 is converted into a bicarbonate trap inside the cell [36]. Different species produce CA in isoforms, some of which remain in cytoplasm while others attach to the cell membrane. Different types of CA, i.e., α, β, γ, δ, and ζ, have been reported and these have no sequence similarity and are independently evolved [36]. α-CA is zinc dependent and mainly found in mammals in the forms of monomer. β-CA is present in plants, algae, bacteria, and archaea and exists as a diamer, tetramer, or hexamer. γ-CA is commonly present in single cell microbes in a trimer form and uses iron and cobalt as cofactors. δ and ζ-CA are found in diatoms and use Cd^{2+} in the place of Zn^{2+} as the marine environment lacks zinc [37,38]. CA performs the reaction over two steps. The first step involves nucleophilic attack of the zinc-bound hydroxide ion on the CO_2 and during the second step an active site is regenerated though the ionization of a zinc-bound water molecule and the removal of a proton from the active site [39]. Conversion of CO_2 into bicarbonate has been reported using free cells, enzymes, and immobilized systems [40]. Different researchers have investigated *Escherichia coli* cells expressing CA on their surface or in periplasmic space for CO_2 capture. Jo et al. engineered *E. coli* to overexpress the CA of *Neisseria gonorrhoeae* in its periplasmic space in soluble form and the engineered strain showed a distinct ability to hydrate CO_2 as compared to the CA expressed in the cytoplasm [41]. CA expressed in a periplasmic space is more stable but has a lower activity because of the presence of an outer membrane barrier [42]. Watson et al. engineered *E. coli* cells to express CA on their membrane and performed CO_2 sequestration using a foam bioreactor that provided a large gas–liquid interface for CO_2 absorption and CA further converted it into bicarbonate [43]. In microalgae, RuBisCo is the main enzyme responsible for CO_2 capture, but it has low selectivity towards CO_2 as compared to O_2 and requires a high CO_2 concentration for O_2 inhibition. Lin et al. overexpressed CA in *Chlorella sorokiniana* and *Chlorella vulgaris* to increase their CO_2 capture potential [44]. The engineered microalgae were cultured in a two layer photoreactor and achieved high biomass and protein production. Desorption of gas and regeneration of solvents requires a heating step and because of temperature sensitivity CA might be recovered from the solvent before heating. Immobilization of enzymes presents an alternative to this additional step (Table 2), but may result in decreased activity because of a mass transfer limitation [45]. Migliardini et al. reported a biomimetic approach for CO_2 capture using thermostable CA purified from *Sulfurihydrogenibium yellowstonense* YO3AOP1 and immobilized on polyurethane foam. A bioreactor containing polyurethane immobilized CA was fed with mixed gas, and the immobilized system captured CO_2 and converted it into carbonate [36]. The activity and stability of CA are the main issues in this method. To overcome these concerns, Zhang et al. embedded CA into zeolitic imidazolate framework (ZIF-L) nanoparticles to synthesize a novel CA/ZIF-

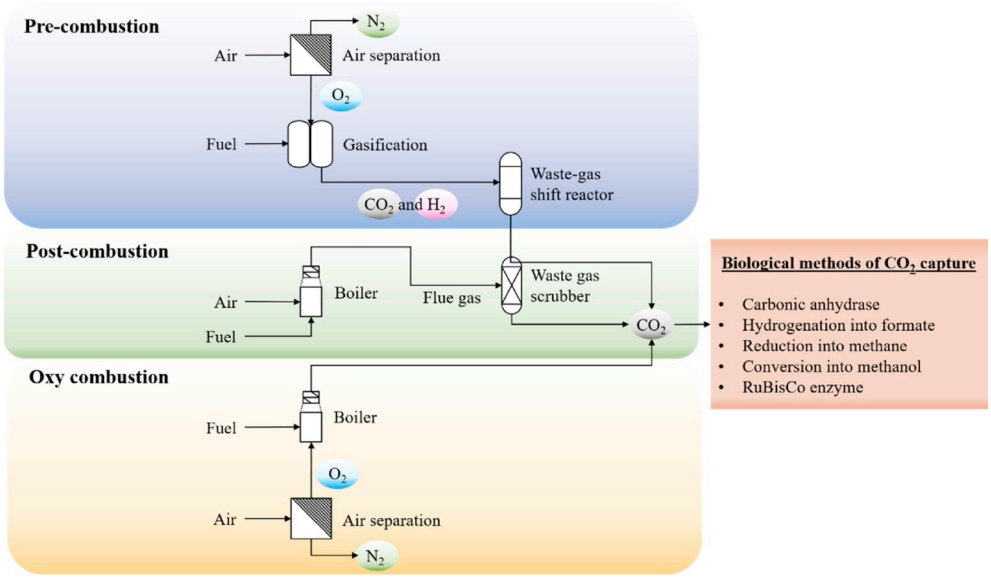

Fig. 2. Different steps and strategies for CO_2 capture involving biological methods.

Table 2
Different matrices/supports reported for carbonic anhydrase (CA) immobilization.

Matrix/support	Substrate/analytical method/function	Remarks	References
Polydopamine (PDA)/polyethylenimine (PEI)-polyvinylidene fluoride (PVDF) (CA-m-PVDF) composite membrane	Gas-liquid membrane contactor (GLMC) was used for CO_2 sequestration.	In a bench-scale GLMC setup, a high-efficiency CO_2 absorption flux of 2.5×10^{-3} mol $m^{-2} s^{-1}$ was obtained.	[50]
Organic metallic frameworks (hydrophilic and hydrophobic)	Hydrophilic supports are better than hydrophobic, and retain 70% activity compared to free CA.	Hydrophilic support increases the thermal stability, and CA was active even after heat treatment at 70 °C.	[51]
Magnetic mesoporous silica	Simultaneous precipitation and crosslinking resulted in the formation of crosslinked enzyme aggregates (CLEAs) on the inner and outer surfaces of mesoporous silica.	External CLEA improved the enzyme loading by 32.9%, and the CO_2 bubbling reactor resulted in 6.5-fold higher production of calcium carbonate.	[52]
Magnetic nanogel (MNP-CA nanogel)	Amino and vinyl groups were grafted onto the surface of magnetic Fe_3O_4. Nanoparticles (MNP) using 3-aminopropyltriethoxysilane (APTES) and *N*-acryloylsuccinimide (NAS) and glutaraldehyde and acrylamide were used for the crosslinking and polymerization.	MNP-CA nanogel increased CO_2 absorption 1.45-fold.	[53]
Metal organic frameworks (MOFs) of ZIF-8	Bovine carbonic anhydrase (BCA) was used, and MOFs-ZIF-8 improved gas adsorption.	Immobilization efficiency was greater than 95%, and the yield was 22 times that of the free enzyme.	[54]
Polycationic dendronized polymer with glass micropipettes and fibers	Immobilized BCA activity was tested using *p*-nitrophenyl acetate as the substrate.	Immobilized system was applied as a flow-through system for continuous operation.	[55]
Poly(vinylidene fluoride) (PVDF) membranes	Membrane was modified via 3-aminopropyl triethoxy silane (KH550) or γ-(2,3-epoxypropoxy) propyl trimethoxy silane (KH560).	PVDF-attached CA showed a storage stability of 85 days and retained 85% activity after 10 cycles.	[56]
Hetero-functional supports ([HFS]$CaCO_3$/H_3BO_3/SiO2) containing CA and a Zn complex	Gravimetric and pressure drop experiments were used to demonstrate the CO_2 capture activity.	Immobilized CA was highly stable in the hybrid solvent system, and could be used for up to 15 cycles with 90% residual activity.	[57]
Liposomes composed of 15 mol% 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine-N-(glutaryl) (NGPOPE)	Carboxyl groups of liposomal NG-POPE were activated with 11 mM 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and 4.6 mM N-hydroxysulfosuccinimide (sulfo-NHS).	Carbonic anhydrase-conjugated liposomes (CALs) showed esterase activity (5.5×10^2 free CA molecules per liposome).	[58]
Carrier-free self-assembled peptides	CA fused with self-assembling peptides is assembled into 50–200 nm nanoparticles at a reduced pH.	This technique offered a carrier-free immobilization approach to stabilize and reuse the enzyme.	[59]
Porous polypropylene (PP)	Hollow fiber membranes coated with polyelectrolytes.	Polyelectrolyte coating resulted in reduced pore size and wetting and increased mass transfer.	[60]
Sol-gel alumina matrices	Sol-gel matrix inhibits denaturation motions; hydration shell provides protection to the protein, and the alumina matrix itself absorbs UV light.	This technique enhanced the UV stabilization of the immobilized enzyme.	[61]
TiO_2 nanoparticles and membranes	Biocatalytic membrane can immobilize 700 mg CA per cm^2 nominal membrane area.	Immobilized nanoparticles could be reused up to 20 cycles with marginal loss of activity.	[62]
Crosslinked chitosan-coated magnetic mesoporous silica	Cross linked chitosan coating prevents the leakage of CA.	Immobilized enzyme was easily separated via a facile magnetic separation, and was stable for up to 85 days.	[63]
Glycidoxypropyl-functionalized nanostructured mesoporous silica	Bovine carbonic anhydrase (BCA) was used, and a para-nitrophenyl acetate (*p*-NPA) assay was used to study the CA activity.	Immobilized CA showed higher storage stability and retained 91% of its initial activity for up to 30 days.	[64]
Crosslinked amino-functionalized paramagnetic nanoparticles	Bovine carbonic anhydrase (BCA) was used.	Able to overcome the aggregation and compaction induced by centrifugation and filtration.	[65]
Carbon nanotube (SWNTs) with bound peptides	CA-fused peptide helps in affinity binding.	This technique allowed the development of a bioactive hybrid material without disrupting the native structure.	[66]
Electropolymerized polypyrrole films	Immobilized CA support was studied to improve the instability in the tertiary amine solvent.	Immobilized CA retained 40% of its initial activity after 42 days at 70 °C in an amine solvent, while free CA lost activity in 1 h.	[67]
Chitosan-alginate polyelectrolyte complex (C-A PEC)	*E. coli* MO1 carbonic anhydrase was used in immobilization, and the immobilized CA retained 100% activity for up to 28 days.	Immobilized CA was able to retain 71% activity for up to 6 cycles.	[68]

L-1 composite, which was able to achieve 1.5 times higher CA activity [46]. The use of CA is limited because of its sensitivity to harsh conditions. Alvizo et al. used site-directed mutagenesis to improve the properties of the CA of *Desulfovibrio vulgaris* and the improved CA was able to tolerate temperatures up to 107 °C [47]. Various solvent system have been used to facilitate CO_2 absorption such as ionic liquid, amine solvent, amino acid salt, carbonate, and immiscible solvent [48,49]. Along with use of a solvent system, contact of gas and liquid in absorption and desorption can be further improved using various contacting devices. Different types of devices have been reported to capture CO_2 such as packed bed (PB), rotating packed bed (RPB), and membrane contractor (MC).

2.1.1. Packed bed (PB) and rotating packed bed (RPB)

In PB, flue gas enters from the bottom and leaves from the top. Absorbents enter from the top and leave from the bottom (Fig. 3a) [69]. Immobilized CA transforms CO_2 into bicarbonate that can be precipitated and collected reacting with calcium. Leimbrink et al. immobilized CA on silica beads and filled these beads in Katapak SP bags and packed them in a PB and reported a 7.5-times higher absorption than a PB operated without an enzyme [45]. RPB technology is used to enhance the mass transfer rate between the gas–liquid phase by applying centrifugal force (Fig. 3b) [69]. This technology is also referred to as higee (high gravity), as it able to enhance distillation and absorption to a significant level [70]. Application of centrifugal force increases shear forces, micromixing, and mass transfer which helps to significantly reduce equipment volume [71]. To operate the RPB, flue gas containing CO_2 is pumped at a high pressure from the outer edge and aqueous absorbent is pumped at the inner edge via a distributor. Absorbents move towards the edge under the effect of centrifugal force

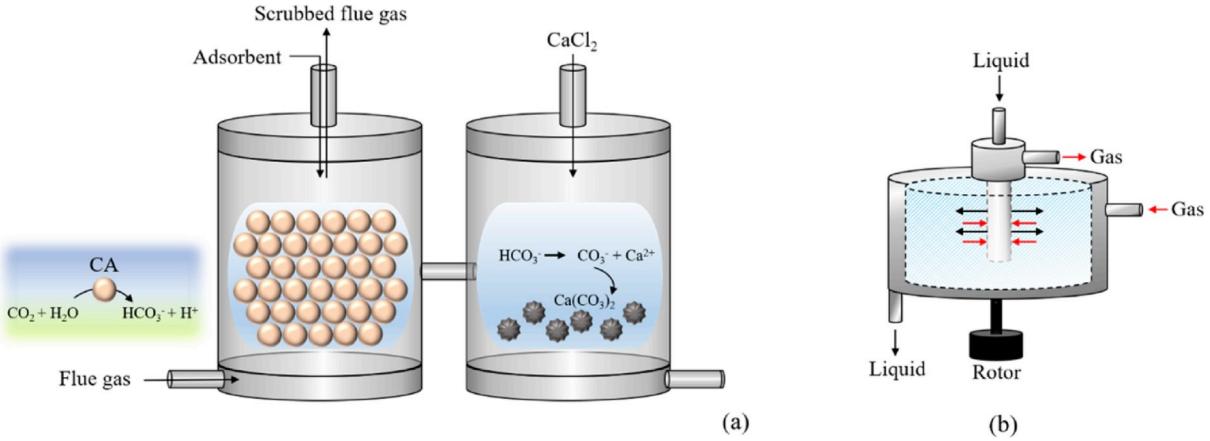

Fig. 3. Design of contacting devices used for biological capture of CO_2 (a) packed bed (PB), (b) rotating packed bed (RPB).

and react with the CO_2 in the gas. The gas leaves the RPB from the top and the absorbent with dissolved CO_2 leaves from the side [70]. Despite 90% CO_2 removal efficiency, this process remains limited to a lab scale.

2.1.2. Membrane contractor (MC)

Membrane contractor technology is a combination of absorption and membrane technology that avoids direct contact between gas and solvent by a membrane barrier (Fig. 4) [69]. Flue gas enters through one side of MC unit and CO_2 permeates through the CA-bound selective membrane, where CO_2 is hydrated into carbonate. CO_2 permeates at higher rate than N_2, CO, and other components of flue gas. CO_2 can be recovered from the other side by high pressure or sweep gas [72]. Use of solvents such as ionic liquids on the other side increases the CO_2 permeability and absorption because of accelerated mass transfer. Materials such as zeolite, ceramic, and silica are used to prepare the membrane. Hou et al. used TiO_2 nanoparticles in immobilized CA, and virgin polypropylene (PP) and superhydrophobic functionalized polypropylene (PP) hollow fiber membranes to prepare an MC and reported reusability of this system up to 10 cycles [73]. Yong et al. used a layer-by-layer technology to engineer polypropylene membranes with carbonic-anhydrase-loaded mesoporous silica nanoparticles and reported CO_2 hydration with increased efficiency of $19 \pm 4\,\mu mol\,cm^{-2}\,min^{-1}$ per layer [74]. Operation of an MC unit requires compression of the flue gas at high pressure before undergoing filtration, which in turn requires additional energy. Furthermore, most of the membranes used are not efficient and selective to CO_2 and thus not suitable for long operation [75]. MC technology can reduce the size of an operating unit by 50–70% as compared to a PB reactor; however, this technology has still not been applied at an industrial scale because of its modular nature and low mass transfer caused by the membrane barrier [69].

2.2. Hydrogenation of CO_2 into formate

Various chemical and biological processes have been reported for CO_2 conversion into formate. A chemical process performed at high temperature and pressure, and requires precious metals as catalysts, which restricts its use [76]. Biological reactions can be performed under mild conditions with high specificity. Reduction of CO_2 into formate has been reported using whole cell catalysis and immobilized enzymes. Various microorganisms have been reported for CO_2 to formate conversion potential, e.g., *Acetobacterium woodii, E. coli,* and *Methylobacterium extorquens* [77–79]. To improve the stability of enzymes and the separation of enzymes, Lu et al. immobilized formate dehydrogenase (FDH) in an alginate silica hybrid gel and used reduced β-nicotinamide adenine dinucleotide (NADH) as an electron donor [80]. The immobilized enzyme showed 95.6% conversion and retained 69% activity after 10 cycles. An electroenzymatic reaction can be used to regenerate NADH. Kim et al. (2014) performed a CO_2 to formate conversion suing *Candida boidinii* FDH and a Cu electrode [81]. Yadav et al. reported an artificial photosynthetic system for NADH regeneration and CO_2 conversion into formate using a graphene-based visible light active photocatalyst-enzyme coupled system [82]. Lee et al. used electrochemically synthesized polydopamine (PDA) thin films copolymerized with an FDH and NADH for CO_2 conversion into formate in which PDA facilitated electron transport and increased the system stability for a long time [83].

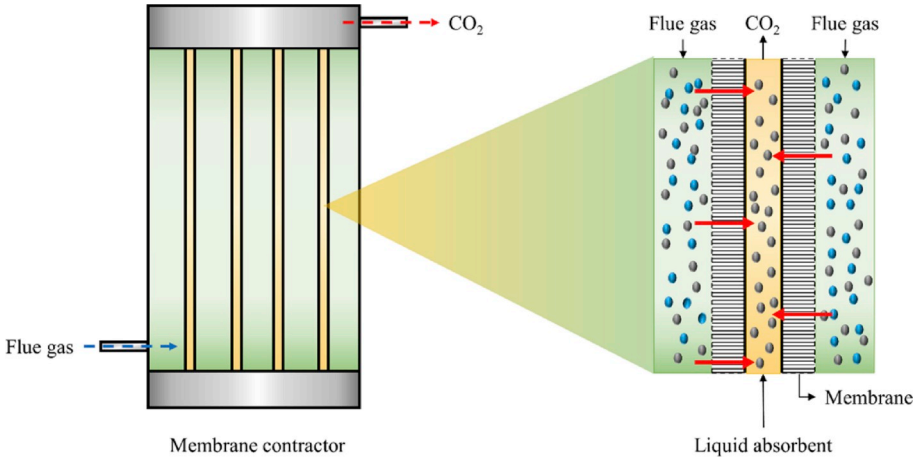

Fig. 4. Membrane contractor design for CO_2 capture.

2.3. Reduction of CO_2 into CH_4

CH_4 production from CO_2 by reduction through a biological process is termed as biogenic methane. ATP dependent nitrogenase is able to conduct a multielectron reduction of an inert molecule [84]. Naturally existing nitrogenase is unable to perform a reduction of CO_2 as several amino acids that approach the FeMo-cofactor also play a role in substrate binding and reduction. Remodeling of nitrogenase by substituting α-195 for Gln and α-70 for Ala enabled it to reduce CO_2 into CH_4 [85]. Fixen et al. developed an anoxygenic phototroph of *Rhodopseudomonas palustris* expressing remodeled nitrogenase and it was able to reduce CO_2 in methane under an in vivo condition in the presence of light [84]. The electrons required for CO_2 reduction were supplied by the Fe protein component of the nitrogenase and the energy was provided by the hydrolysis of the ATP molecule. Light plays a role in regeneration of ATP through cyclic phosphorylation [84].

Another method of CO_2 reduction that has been reported is the microbial electrolysis cell (MEC) [86], which enables simultaneous CO_2 capture and energy production [87]. The MEC system is a modified microbial fuel cell (MFC) in which the applied potential difference at the biocathode (a cathode with a microbial film) leads to the reduction of CO_2 into methane [88]. Although microbes can produce a potential of 0.3 V from the acetate in the anodic chamber, this is less than the potential required to produce hydrogen at the cathode (0.414 V); thus, additional potential must be supplied for hydrogen production [89]. The use of a biocathode can further support the reduction of CO_2 into methane. Biocathodes are a cheaper alternative to costly cathode materials such as platinum. The microorganisms attached to the biocathode can directly accept electrons from the electrode or use electron shuttles and cathodic H_2 to reduce CO_2 to methane [90]. Many studies have been published on this topic, and recent studies are listed in Table 3. Mixed cultures are considered to be more suitable for biofilm production in biocathodes, as they are robust towards environmental stress. Villano et al. suggested that MECs could be combined with existing anaerobic digesters to improve the quality of the biogas by reducing the CO_2 into methane, which is a component of biogas (Fig. 5) [91]. In a recent study, Dou et al. studied a hybrid anaerobic digestion-bioelectrochemical cell (AD-BEC) system at different external potentials, and reported higher methane productivity in the hybrid system compared to the traditional system, as the external potential enriches the exoelectrogens in the anodic biofilm and the hydrogenotrophic methanogens at the cathode biofilm [92].

2.4. CO_2 conversion into methanol using an enzymatic cascade

CO_2 can be reduced into methanol using different catalysts at higher temperatures (150–300 °C) and pressures (3–14 MPa). Enzymatically, these reactions can be carried at room temperature using an enzymatic cascade. The reduction of CO_2 to methanol is conducted via three enzymes step wise and requires NADH in its reduced form as a cofactor. The first reaction step of a conversion of CO_2 to formate (HCOOH) is carried by formate dehydrogenase (FDH), which further converts into formaldehyde (HCHO) and finally into methanol by formaldehyde dehydrogenase (FaldDH) and alcohol dehydrogenase (ADH), respectively. Despite advancement in technology, CO_2 conversion to methanol remains a challenge as enzymes start to lose activity as methanol is produced. Luo et al. investigated co-immobilization and sequential immobilization of FDH, FaldDH, and ADH on flat-sheet polymeric membranes for CO_2 conversion into methanol [101]. The co-immobilization strategy resulted in a lower conversion as a second reaction, i.e., conversion of formic acid to formaldehyde was found to be a bottleneck. Sequential immobilization is the preferred method in multi-enzymatic reaction as each step can be controlled [101]. Three moles of NADH were required to produce 1 mol of methanol from CO_2, which affects the economics of the process [102]. Aresta et al. reported a hybrid enzymatic/photocatalytic process for simultaneous conversion

Table 3
MECs with various biocathodes for the reduction of CO_2 into methane (table updated and adapted from Ref. [88]).

MEC type	Cathode material	Biofilm	Voltage (V) versus SHE	Columbic efficiency (%)	Anode properties	Methane production	References
Single chamber	Graphite felt	Mixed methanogenic cultures	0.5–0.2	–	Graphite felt	105 vs. 84 mL/(L·d)	[92]
Single chamber	Graphite rod	Mixed methanogenic cultures	0.6	–	Graphite rod	0.067 mmol/d	[93]
Dual chamber	Carbon felt	Mixed methanogenic (MM) culture and enriched hydrogenotrophic methanogenic (EHM)	−0.8	62 and 98	Carbon felt	0.586 ± 0.029 mmol CH_4 per mg biomass per day	[94]
Single chamber	Carbon cloth	Mixed culture	0.8	–	Graphite brush	91.8 g CH_4 per m^3 reactor per day	[95]
Dual chamber	Carbon cloth	Methanothermobacter-related methanogen and synergistetes	0.2–0.5	> 90	Carbon cloth	1103 mmol/(m^2·d)	[96]
Dual chamber	Carbon sticks	Anaerobic sludge suspensions	−0.9	24.2	Carbon sticks	2.30 ± 0.34 mL	[90]
Single chamber	Graphite plate	Methanobacterium	0.7	< 100% (bog sample) and > 100% (AD)	Graphite plate	0.27 mL/(mL·cm^2)	[97]
Dual chamber	Graphite rod	Hydrogenotrophic methanogens	−0.7	80–85	Graphite Rod	1 mmol CH_4	[98]
Dual chamber	Stainless steel with platinum coating	Mixed methanogenic cultures	−0.78	75	Graphite fiber brush	0.60 ± 0.01 mol-CH_4 per mol-acetate	[99]
Dual chamber	Carbon felt	Mixed methanogenic cultures	0.95–0.65	60–100	Carbon felt	129.32 mL/d	[100]
Single chamber	Graphite granules	Mixed methanogenic cultures	+0.5 anode	~100	Graphite granules with *Geobacter sulfurreducens*	0.018 L/(L·d)	[91]

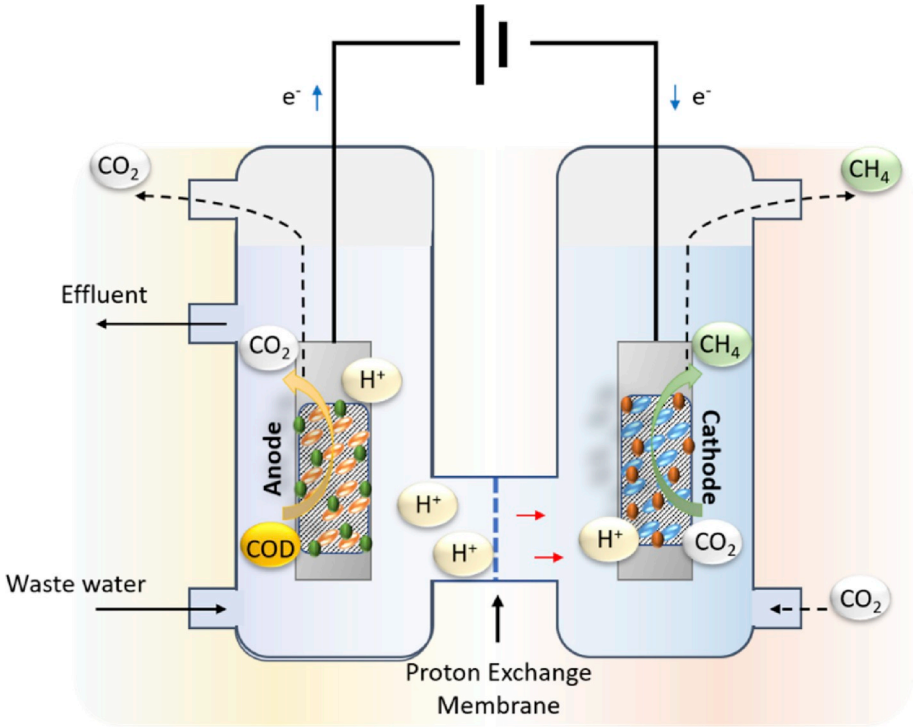

Fig. 5. Diagram showing a hybrid anaerobic digestion-bioelectrochemical cell for simultaneous wastewater treatment and CO_2 reduction into methane.

of CO_2 into methanol and regeneration of NADH from NAD^+ using a TiO_2-based photocatalyst [103]. Using this cofactor regeneration technology, they were able to produce 100–1000 mol of methanol from one mol of NADH. Marques et al. used glutamate dehydrogenase (GDH) for coenzyme NAD^+/NADH regeneration. GDH immobilized on the functionalized magnetite nanoparticles along with three cascade enzymes were required for CO_2 conversion into methanol, and the reaction carried by these four enzymes resulted in a 64-times conversion [104]. Ji et al. reported an artificial photosynthesis system for bioconversion of CO_2 into methanol [105]. A cascade enzyme reduction system coupled with a GDH coenzyme regeneration system was encapsulated into a polyelectrolyte-doped polyurethane (PU) nanofiber lumen having a molecular weight cut off of 20 kDa to avoid leaking of encapsulated enzymes and facilitate the mobility of polyelectrolyte poly(allylamine hydrochloride) (PAH) [105]. Compared to the solution-based system artificial photosynthesis system, it resulted in an increase in methanol production of 35.6%–90.65%. Schlager et al. developed a coenzyme-independent method for direct conversion of CO_2 into methanol by immobilizing formate, formaldehyde, and alcohol dehydrogenases on an electrode using an alginate-silicate hybrid gel matrix and supplying an electron directly to the immobilized enzymes through an electrode [106].

2.5. Involvement of the RuBisCo enzyme

Ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCo) is selective to substrates, i.e., CO_2 and O_2. As a carboxylase, it catalyzes carboxylation of ribulose-1,5-biphosphate and produces a highly unstable six-carbon phosphorylated intermediate known as 3-keto-2-carboxyarabinitol-1,5-bisphosphate, which further produces glucose. As an oxygenase, it initiates C_2 photorespiration, produces 2-phasphoglycolate, and releases CO_2 [107]. RuBisCo shows lower specificity towards CO_2 over O_2 which is the main cause of the low CO_2 fixation rate. Researchers are working on the engineering of RuBisCo but have only been able to obtain limited access as an increase in activity has resulted in its decreased specificity towards CO_2, and vice versa, an improvement in specificity causes a decrease in its activity [108]. The ratio of specificity towards CO_2 and O_2 is represented by the S_{rel} value. Mainly two types of RuBisCo, red and green, have been reported. Ninomiya et al. analyzed the protein structure of these two RuBisCo and reported that the red type of RuBisCo has a high S_{rel} (238) because of a latch-like structure formed between the oxygen of Val 332 and the side chain amide nitrogen of Gln 386 [109]. Liang and Lindblad overexpressed RuBisCo in *Synechocystis* PCC 6803 and the improved strain showed increased growth and photosynthesis activity [110].

3. Biological conversion of CO_2 into bioenergy

CO_2 captured from different stationary sources (coal-fires plants, cement, and steel factories, etc.) can be stored for later use or used directly as feedstock for microbial fermentation to produce energy (biodiesel, bioalcohol, and advanced fuel) (Table 4).

3.1. Biodiesel

CO_2 directly or its other derivatives (methane and formate) can be used as a carbon source to produce biodiesel. Various bacterial (*Bacillus cereus, Bacillus subtilis, Myxococcus xanthus, Pseudomonas aeruginosa*), and algal (*Botryococcus braunii, Chlorella Kessleri, Chlamydomonas, Chlorocuccum littorale, Chlorella vulgaris*) strains have been recognized for carbon capturing and its precipitation as calcium carbonate [107,108,111–114]. Microalgae are receiving considerable attention as they are able to directly fix CO_2 from the atmosphere or soluble carbonates, cultivated in non-agricultural land using wastewater, and provide a high lipid yield [115–117]. Wastewater is rich in nitrogen and phosphorus, and the culture of algal species utilizes these and helps to remove ammonia, nitrate, and phosphate from the wastewater. An algal culture system is classified as an open or closed system. An open culture refers to algal cultures in ponds, lagoons, and shallow circulating water channels, while in a closed system algae is cultured in transparent walled vessels (photobioreactor) under controlled conditions [116]. Microalgae can fix CO_2 10–15 times faster than plants and have no dilemma regarding a food and fuel issue. Algae fixes CO_2 using an oxygenic photosynthesis method or through the involvement of the

Table 4
Different microorganisms able to capture and transform CO_2 into bioenergy.

Category	Microorganism	Comment	CO_2 fixation rate (g/(L·D))	Productivity (mg/(L·D))	References
Biodiesel	*Bacillus* sp. SS105	Bacterial strains were isolated from a free air CO_2 enrichment (FACE) soil area.	0.287	1.7	[138]
	Asterarcys sp.	Able to grow under wide range of pH values.	–	30	[139]
	Chlamydomonas sp. JSC4	A marine alga able to grow at 3.5% salinity.	–	169	[140]
	Chlorella pyrenoidosa SJTU-2	Able to grow at a higher concentration of CO_2 (30–50%) and polyunsaturated fatty acid content increases with the increase in CO_2 concentration.	0.260	29.57	[141]
	Chlorella sp. BTA 9031	Optimum lipid content was observed at 4% CO_2.	0.235	21.3	[142]
	Chlorella vulgaris	5% CO_2 is most suitable for optimal growth.	–	157	[21]
		Bubbling-type photosynthetic algae microbial fuel cell was used.	0.605	105.9	[143]
		Vertical tubular photobioreactor was used for the cultivation of algae.	0.43	430	[144]
		Air-lift microbial fuel cell was used for CO_2 fixation and bioenergy production.	1.29	234.3	[145]
	Chlorella vulgaris NIOCCV	Cultivated in seafood processing industry wastewater with a continuous supply of 10% CO_2.	0.43	92	[146]
	Coelastrum sp. SM	Cultivated in an air-lift photobioreactor under a high CO_2 (12%) concentration.	0.302	101	[147]
	Moorella thermoacetic and *Yarrowia lipolytica*	First strain converts CO_2 and CO or H_2 into acetic acid, and the second strain converts acetic acid into lipids.	–	4560	[148]
	Neochloris oleoabundans	N/P ratio affects the biomass and lipid production.	–	45	[149]
	Nannochloropsis sp.	Able to grow at 15% CO_2.	–	18.93	[150]
	Scenedesmus bajacalifornicus BBKLP-07	Cultivation was performed at a 1 L scale, and maximal CO_2 fixation occurred at 15%.	0.12	15.7	[29]
	Scenedesmus obliquus CNW-N	Two-step cultivation strategy was used for the cultivation.	0.549	78.73	[151]
	Scenedesmus obliquus SJTU-3	High concentration of CO_2 is favorable for polyunsaturated fatty acid accumulation.	0.288	32	[141]
Ethanol	*Moorella* sp. HUC22-1	Produces ethanol from H_2 and CO_2 at 55 °C.	–	50	[152]
n-butanol	*Synechococcus elongatus* PCC 7942	Algae was engineered with oxygen tolerant CoA-acylating aldehyde dehydrogenases (PduP).		51	[153]
Isobutanol	*Ralstonia eutropha* H16	Uses integrated system to convert CO_2 into formate electrochemically which further converts it to isobutanol by engineered *R. eutropha* H16.	–	206	[154]
	Synechococcus elongatus PCC 7942	Strain was engineered by replacing oxygen-sensitive CoA-acylating butyraldehyde dehydrogenase (Bldh) with oxygen-tolerant CoA-acylating aldehyde dehydrogenases (PduP).	–	51	[153]
1,3 propanediol	*Synechococcus elongatus* PCC 7942	Conversion was performed without the addition of coenzyme B_{12}.		20	[133]
2,3 butanediol	*Synechococcus elongatus* PCC7942	Strain engineered for 2,3-butanediol synthesis pathway along with a cofactor biosynthesis pathway.	–	793	[155]
		Glycolytic pathways and the Calvin-Benson cycle were modified to increase carbon flux and redirect it towards carbon fixation.		1100	[156]
Ethylene	*Synechocystis* sp. PCC 6803	Engineered with an *efe* gene encoding an ethylene-forming enzyme from *Pseudomonas syringae* pv.	–	171	[157]
Isoprene	*Synechocystis* sp. PCC 6803	Engineered by an isoprene synthesis gene from *Pueraria montana*.	–	0.050	[158]
Limonene	*Synechocystis* sp. PCC 6803	Engineered with plant limonene synthase.		0.056	[159]

zinc-dependent CA enzyme. CA converts CO_2 into bicarbonate and this is transported inside the cell through a specific transporter [118]. Most of these microalgae can grow under a low concentration of CO_2 (5%). For industrial potential, microbes should be able to grow at a higher CO_2 concentration. Microorganisms can be engineered to improve CO_2 capture capacity and increase the oil accumulation potential. Li et al. used a chemical mutagenesis method to improve the CO_2 tolerance level of *Synechococcus obliquus* WUST4, and directly developed a pilot-scale CO_2 fixation system from discharge of a combustion chamber [20]. Lee et al. engineered *Synechococcus elongatus* PCC 7942 with an ethanol producing pathway and ester synthase (AftA); the modified organism was able to produce fatty acid ethyl ethers (FAEEs) directly from CO_2 [119]. The integration of CO_2 capture with other technologies, such as wastewater treatment, may help to reduce the environmental pollution from the greenhouse gases released during the anaerobic digestion process [120]. Rosli et al. developed an integrated approach for simultaneous wastewater treatment and CO_2 capture [121]. *Chlorella vulgaris* was cultured on a polyurethane support material in a fluidized bed reactor to facilitate the microalgal harvesting [121]. Microbes are cultured using CO_2 feedstocks which are harvested to collect biomass which is further used for biodiesel production as it contains lipids. Extracted lipids can be converted into biodiesel using a transesterification reaction with alcohols carried by enzymatic and chemical catalysts [122].

3.2. Ethanol

Most of alcohol production processes are based on fermentation of agricultural crops (corn, sugarcane, and sorghum). Because of limited arable land and a food security issue, further development of this process is hampered. Photosynthetic cyanobacteria appear as a potential candidate for bioalcohol production as they have the capability to capture CO_2 and convert it into organic compounds through a Calvin cycle using solar energy [123]. These strains can be engineered to add to the bioalcohol production pathway. According to a theoretical calculation, 5280 gallons per acre per year of ethanol can be produced using photosynthetic organisms, while annual yield of ethanol from corn is 321 gallons per acre per year and from sugar cane is 727 gallons per acre per year [124,125]. Deng and Coleman were the first to report autotrophic ethanol production in the *Synechococcus* sp. strain PCC 7942 by heterologous expression of pyruvate decarboxylase (PDC) and ADH from *Zygomonas mobilis* [126]. Gao et al. similarly engineered *Synechocystis* sp. PCC6803 by heterologously expressing PDC and ADH and disrupting various genes involved in PHA synthesis, they were able to produce 5.50 g/L ethanol. In cyanobacteria, the Calvin-Benson-Bassham (CBB) cycle is the main pathway involved in CO_2 fixation [123]. Liang et al. engineered *Synechocystis* PCC 6803 by overexpressing four genes from the CBB pathway with ethanol-producing genes [127]. Silva et al. used flow cytometry to evaluate the ethanol tolerance of *Synechocystis* PCC 6803. They found that the produced bioethanol must be extracted from the culture to avoid detrimental effects on the biomass [128]. Alcohol dehydrogenase (AdhA) is the main enzyme involved in ethanol tolerance. Its deletion reduces the survival of microalgae in the presence of ethanol (4% v/v) [129]. NADPH plays an important role in conversion of acetaldehyde to ethanol. Velmurugan et al. developed a metal oxide mediated NADPH regeneration system that was able to double the ethanol content compared to the control [130].

3.3. Other advanced biofuels

1-butanol is a potential biochemical and fuel which is largely produced by using *Clostridium* or other engineered strains. Naturally, cyanobacteria are not able to produce 1-butanol. Lan and Liao (2011) introduced a coenzyme-A independent butanol synthesis pathway in *S. elongatus* PCC 7942 and first demonstrated autotrophic 1-butanol production [131]. The same research group reported production of energy dense biofuel 2-methyl-1-butanol (2 MB) in *S. elongatus* PCC 7942 [132]. A total of 2 MB production is well reported in recombinant *E. coli* through the isoleucine pathway by decarboxylation of 2-keto-3-methylvalerate followed by reduction. Miao et al. engineered *Synechocystis* sp. PCC 6803 by expressing α-ketoisovalerate decarboxylase from *Lactococcus lactis* and different ADHs for isobutanol production [132]. Shen et al. introduced a citramalate pathway to produce isoleucine precursor 2-ketobutyrate and the genes ketoacid decarboxylase (*Kivd*), and alcohol dehydrogenase (*YqhD*); they reported 20 mg/L of 2 MB production [132]. Kusakabe et al. engineered an isopropanol synthesis pathway in *S. elongatus* PCC 7942 by introducing acetyl-CoA acetyl transferase [55], acetoacetyl-CoA transferase (*atoAD*), acetoacetate decarboxylase (*adc*), and secondary alcohol dehydrogenase (*adh*); they reported 26.5 g/L of isopropanol production over 9 days [133].

Cyclic hydrocarbons are a component of petroleum fuel and can improve its performance [134]. Limonene, a cyclic monoterpene, is generally produced by plants and has similar properties as biodiesel and jet fuel. Halfman et al. engineered the cyanobacterium *Anabaena* sp. PCC 7120 to produce and secrete limonene by introducing limonene synthesis genes from Sitka spruce [134]. Alka(e)nes, an advanced biofuel, was produced by Wang et al. by overexpressing native genes acyl-acyl carrier protein reductase and aldehyde-deformylating oxygenase in *Synechocystis* sp. PCC 6803 [135]. Yao et al. engineered *Synechocystis* sp. PCC 6803 for fatty alcohol production by heterologously expressing the fatty acyl-coenzyme A (acyl-CoA) reductase gene from *Marinobacter aquaeolei* VT8 bacterium and deleting the aldehyde-deformylating oxygenase gene involved in alkene production [136]. Levulinate is a byproduct of the *in situ* transesterification process of microalgae, and is also used as a fuel additive. Algae rich in carbohydrates lead to a higher production of levulinate [137].

4. Alternate methods of CO_2 capture

Along with biological CO_2 capture methods, there are other methods that have also been reported such as the a) absorption, b) adsorption, c) cryogenic, and d) membrane methods. Absorption is the only technology available for commercial purposes while the other technologies are at the developing stage.

4.1. Absorption

Two types of absorption processes, i.e., chemical and physical absorption, have been reported. During chemical absorption, CO_2 is captured at a low pressure and temperature (40–60 °C) using solutions such as alkanolamine (monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA)), 2-amino-2-methyl-1-propanol (AMP), piperazine (PZ), potassium carbonate (K_2CO_3), and sulfolane [160,161]. Primary and secondary amine react with the CO_2 to form carbonate and tertiary amine to form bicarbonate [162]. The amine serves as a buffering agent for the reaction solution, a chelating agent for the metal ions, and an activating agent for CO_2 [163]. This technology is used to capture CO_2 from low concentration flue gases. CO_2 reacts with the solution to form a loosely bound intermediate compound. The addition of PZ to an aqueous solution of AMP promotes the CO_2 absorption rate only if the partial pressure of CO_2 is high, while at low pressures it has a negative effect [164]. Then, the captured CO_2 can be easily recovered by applying heat (100–140 °C), and the regenerated solvent can be reused in the process. During physical absorption, CO_2 is captured at a high pressure and low temperature, and heat is applied to recover the CO_2 and regenerate the solvent. This process is applied to flue gases containing 35–40% CO_2, and a physical solvent such as Selexol consisting of dimethylethers of polyethylene glycol is used [165]. Belaissaoui et al. developed an integrated gasification combined cycle (IGCC) technology to capture CO_2 from the gasification of carbonaceous fuels, in which a skin hollow fiber gas-liquid membrane contactor was packed with a pressurized physical solvent

(Selexol). The authors reported that the energy required for absorption and desorption was half that of other reported technologies [166]. This process also had some disadvantages, such as its high power requirements for CO_2 recovery and solvent regeneration, need for corrosion control, and reduced efficiency due to the presence of other gases such as NO_x and SO_x [165].

4.2. Adsorption

During adsorption, carbon capture occurs through interaction with a solid surface such as activated charcoal and an adsorbing bed of alumina and zeolite. Mainly, three types of adsorption processes have been reported, i.e., i) temperature swing adsorption (TSA), ii) pressure swing adsorption (PSA), and iii) electric swing adsorption (ESA) [167]. These processes can be classified according to the methods used to recover CO_2 and regenerate the adsorbent material; in TSA, temperature is used; in PSA, pressure is applied; and in ESA, regeneration is completed by passing a low-voltage electric current through the adsorbing material. A novel hybrid zeolite/activated carbon honeycomb able to perform ESA adsorption was combined with vacuum swing adsorption (VSA) to capture CO_2. The combined process resulted in a CO_2 recovery of 72% with 33% purity within a short electrification time of 30 s under a mild operating pressure (10 kPa) [168]. Hong et al. developed a microporous carbon compartment via the controlled carbonization of wheat flour, and reported that it achieved a CO_2 capture of 5.70 mol/kg at 0 °C and 3.48 mol/kg at 25 °C [169]. Amine-impregnated adsorbents can be used to capture CO_2 from dilute flue gas. Peng et al. prepared a mesoporous carbon material from chitosan impregnated with pentaethylenehexamine; the synthesized material showed high adsorption and selectivity for CO_2 [170]. Covalent organic polymers (COPs) are a new class of adsorbent that has recently been reported. COPs have high hydrothermal stability, good chemical tuning flexibility, and low cost. This adsorbent showed good performance in the removal of CO_2 from natural gas [171]. To capture CO_2 directly from atmospheric air, Sujan et al. functionalized polymer/silica fibers with a primary amine (poly (ethylenimine)) sorbent, which resulted in production of high purity CO_2 from both dry and humid ambient air mixtures [172]. Ramadass et al. explored naturally available halloysite nanotubes (HNTs) and HNT/Kaolin mixtures for CO_2 adsorption, and reported CO_2 capture of 120 μmol/m^2, which is relatively higher than that of existing well-known commercial materials, such as activated carbon, mesoporous silica, and carbon nitride materials [173]. The increased CO_2 adsorption was due to the excellent surface and tabular morphology of their pores, and the presence of free hydroxy groups on the inner and outer surfaces of the HNTs.

4.3. Cryogenic method

Cryogenic CO_2 capture technology is based on condensation and cooling principles. In this technology, CO_2 is cooled at a lower temperature (−100 to −135 °C) to change it to a solid and separate it from other gases [174]. The solid CO_2 is further pressurized, melted, and transported as a liquid. This process is applied to recover CO_2 when a gas mixture consists of more than 50% CO_2 content as this process requires energy for refrigeration affecting the economics of the process if used to dilute CO_2 streams [175]. The main advantage of this process is no requirement of any chemical absorbent and it can be performed at a lower pressure. During this process, CO_2 is directly converted into a liquid which making its transport through a pipeline easy. The water content in the gas mixture used to recover the CO_2 should be limited as at a low temperature water forms ice and plugs the system, further reducing process efficiency. Stirling cooler technology, which is based on differences in condensation and desublimation, was utilized by Song et al. (2012). H_2O and CO_2 condensed and desublimated in different parts of the capture system, avoiding need to use solvents or apply pressure [176]. The Stirling technology was improved through integration with heat exchanger networks, in which the heat associated with the separated stream (condensed water, residual gas, and captured CO_2) was recovered and used to run the unit [177]. Using this technology, the authors were able to reduce the power consumption of the CO_2 capture unit from 195.29 MW to 88.0 MW [177]. Knapik et al. developed an integrated approach for the removal of CO_2 from flue gas produced during oxy combustion, in which N_2 from the nitrogen removal unit was used to cool the condenser for CO_2 liquification [178].

4.4. Membrane technology

In membrane-based technology, a partially permeable membrane separates CO_2 from a gas mixture. This technology is preferred for low-carbon-emission plants as it can be continuously performed. The main driving force for the gas separation is a difference in partial pressure between the feed and permeate sides [179]. Membrane materials are generally divided into three types: (i) ceramic, (ii) polymeric, and (iii) hybrid membranes [180]. The use of various ceramics (comprising an inorganic material such as silica, graphene oxide, or alumina) and a polymeric membrane (comprising polypropylene (PP), nylon, polytetrafluoroethylene (PTFE), of polyvinylidene fluoride (PVDF)) has been reported for CO_2 capture. Polymeric membranes usually operate at lower temperatures, have good mechanical properties, and can be more easily manufactured with large areas [180]. Ceramic membranes have higher chemical and thermal stability, but their surfaces are more hydrophilic, resulting in wetting problems. Additionally, it is difficult to manufacture ceramic membranes with large surface areas [181]. Qu et al. prepared a novel polyelectrolyte membrane (quaternary ammonium polysulfonate) to achieve increased CO_2 permeability. The hydrophilic quaternary ammonium groups formed ionic cluster under humidified conditions, and further promoted the selective transport of CO_2 over CH_4 [182]. Xu et al. prepared a mixed matrix membrane (MMM) by crosslinking UIO-66-NH_2 nanoparticles on poly(vinylamine) (PVAm) [183]. The fabricated MMMs showed excellent gas separation and long term stability towards flue gas [183]. The use of hybrid composite membranes to increase CO_2 capture has also been studied. Lim et al. prepared a hybrid composite membrane using poly(vinyl benzene chloride) (PVBC) beads functionalized with an ionic liquid (bis (trifluromethane)sulfonimide (BITFSI)). The hybrid PVBC-BITFSI membrane had high selectivity towards CO_2 due to the ability of beads to control the diffusivity and solubility [184]. The use of nanocellulose as an additive in a poly(vinyl alcohol) (PVA) nanocomposite for CO_2/N_2 separation has also been demonstrated. The addition of nanocellulose improved the CO_2 permeance (127.8 ± 5.5 GPU) and increased the CO_2/N_2 separation factor (39 ± 0.4) of the PVA composite membranes [185].

5. Challenges in CO_2 capture and transformation into energy

5.1. Challenges in CO_2 capture

The main obstacle to implement this technology is cost; it requires government policies and subsidies to accelerate its implementation. Next is the link between CO_2 capture and its transformation into resource; these technologies are still at an initial stage and require considerable research input to make them a reality. Another challenge is the lack of cooperation among professionals, as CO_2 capture, and its conversion into resources, are two individual and independent processes [186]. These two technologies need to be integrated to reduce the cost of CO_2 storage and transportation. There are other technological challenges as well, as solvent absorption is the only technology available at a commercial scale and involves solvent regeneration and CO_2 compression which consumes considerable energy. Therefore, construction of plants with CO_2 capture technology will be costly and thus there is a need to find new CO_2 capture technologies as other alternative reported technologies (biological CO_2 capture and membrane

Table 5
Technical challenge and limitation of various CO_2 capture technologies.

Technology	Technical challenges and limitations	References
Carbonic anhydrase (CA)	Major challenges during the reactor-based process are poor mass transfer and the formation of H_2CO_3,- which inhibits enzyme activity. Backward dehydration is also a challenge. New immobilization materials to improve the stability and reusability of the enzyme are required. Carbonate formation requires an alkaline pH, so alkaliphilic CA must be identified. Heat treatment is required for CO_2 recovery and solvent regeneration which results in CA inactivation.	[36,191]
Hydrogenation and reduction of CO_2	These reactions require cofactors, which increases the production cost. Either an efficient cofactor regeneration system or a cofactor independent process involving direct transfer of the electrons to the electrode must be developed. More suitable matrices able to immobilize multiple enzymes together without affecting the activity of each must be identified.	[82,106]
Microbial electrolysis cell (CO_2 reduction to CH_4)	More efficient electrodes must be developed, as the two-dimensional structure of the electrode limits the available surface area and results in low electrocatalytic activity. Very limited information is available on hybrid AD-MEC systems operation and scale-up; this research area should be further explored. Cathode potential must be regulated, as different products are formed at different potentials.	[88,192]
RuBisCo Enzyme	Specificity and activity of RuBisCo towards CO_2 over O_2 must be improved.	[108]
Chemical absorption	To make CO_2 capture cost effective, absorbents that require low energy for regeneration and have a high absorption capacity and low heat of reaction must be found. CO_2 loading is low in amine-based absorbents due to the formation of stable carbamates. Potassium carbonate absorbents require promoting amines (piperazine) and corrosion inhibitors when used in carbon steel.	[160,161]
Adsorption	Materials have low adsorption rates and poor CO_2 selectivity. Sorbent degradation occurs during the recycling process, and it is difficult to work with the solid material.	[193,194]
Cryogenic method	Cryogenic processes require substantial energy (*i.e.,* 80% for CO_2 capture, 10% for transportation, and 10% for storage). Process depends on the availability of natural gas. Process is only applicable to flue gas with high CO_2 contents (> 20%) and very low moisture.	[195]
Membrane separation	Process is still not cost effective, as energy is required to compress the flue gas and create the driving force for gas transport and post-cleaning operation. Membrane stability is an issue; the membrane loses stability in the presence of flue gas contaminants and higher temperatures. Mechanically robust, ionic liquid stable membranes must be developed.	[196]

separation) are in their initial stages. CO_2 capture from low-concentration flue gas is costly and these technologies can be applied to only coal-fired plants which emit flue gas containing more than 15% CO_2 [187]. Impurities present in the flue gas (NO_x and SO_x) reduce the efficiency of the CO_2 separation and capture process. Development of a process that can pretreat flue gas and simultaneously capture CO_2 will help to reduce the cost. In spite of extensive research, further work remains in many areas in order to make CO_2 capture technology more efficient (Table 5).

5.2. Challenges in CO_2 to bioenergy conversion

CO_2 is seen as waste, but it can be converted into a resource if properly managed. CO_2 transformation into energy using a biological system is a possible solution to reduce its emission into the atmosphere and reduce greenhouse gas levels. CO_2 concentration, pH, and temperature are the main factors affecting the CO_2-to-bioenergy conversion process. CO_2 concentration affects microbial CO_2 reduction efficiency, and most microalgae show a maximum efficiency at 2–5% CO_2 [188]. There is a need to improve microbes in terms of their tolerance of CO_2 and an increased reduction rate. Most of the biological processes are performed at ambient temperature (15–26 °C), while flue gas is emitted at a higher temperature and should be cooled before subjection to a biological system [189]. There is a need to search for microbes that can perform at a higher temperature as flue gas temperatures reach as high as 120 °C. Moreover, pH is also an important parameter for microbial growth, as most microbes grow near a neutral pH. For higher productivity, there is need for CO_2 feeding at a higher concentration; however, an increase in CO_2 concentration results in a decrease in pH (5) that can adversely affect microbial growth [190]. Thus, it is very important to balance pH during the process. These are the main challenges that need to be focused on to make the CO_2-to-bioenergy concept a reality.

6. Process design to improve the CO_2-to-bioenergy conversion

Reviewing the different available CO_2 capture and bioenergy production technologies, we considered that the following two technologies may improve the economics and efficiency of the CO_2-to-bioenergy technology.

6.1. Electrical-biological hybrid system

CO_2 is an abundantly available feedstock and can be converted into various industrially important chemicals such as acetic acid, polyhydroxyalkanoates, and biofuels [197,198]. It is a very stable molecule and its reduction requires a high input of energy to carry out multi-electron reduction steps. A biological method of CO_2 reduction is an attractive approach as it can be performed at an ambient temperature and pressure and biological catalysts have a self-regeneration capability and are suitable for long run performance [23]. Equations (i) to (v) show the possible routes for reduction of CO_2 into various fuels along with the corresponding theoretical potential required to carry the reaction [106]. To overcome this energy barrier and convert CO_2 into biofuel, catalysts are required.

Various dehydrogenases have been reported to carry these reactions and require the cofactor NADH as an energy carrier to reduce the CO_2. For each step of a two-electron reduction of CO_2, one molecule of NADH is oxidized into NAD^+. Although an enzymatic reaction can be performed at an ambient temperature and pressure, the addition of NADH affects the economics of the process. Development of a coenzyme-independent process for reduction of CO_2 to biofuel is the main challenge

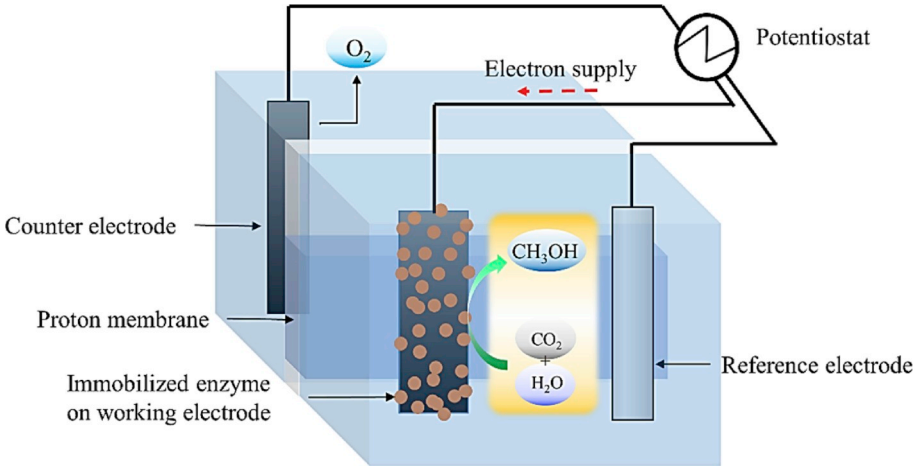

Fig. 6. Process design of an electrochemical reduction of CO_2 into methanol.

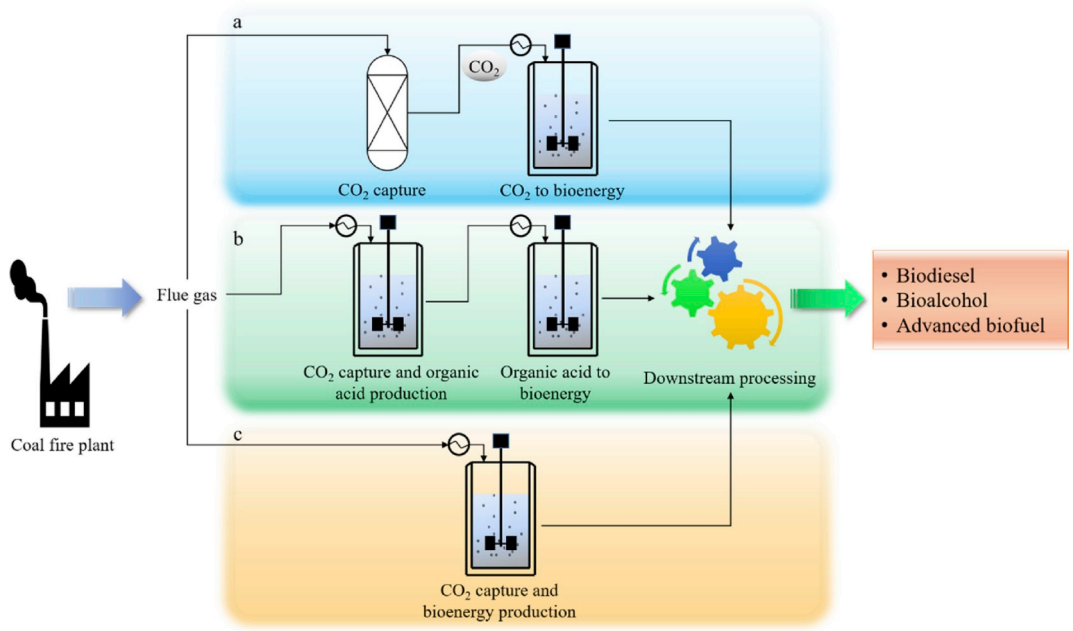

Fig. 7. Process design for CO_2-to-bioenergy conversion, a) CO_2 captured from a coal-fired plant and further used in fermentation, b) CO_2 captured and transformed into volatile fatty acids that are further used for bioenergy production, c) single-step process involving simultaneous CO_2 capture and bioenergy production.

and various research groups are working on this issue. To overcome the cost and cofactor issues, an electrochemical process is a possible solution that involves direct injection of electrons into the enzyme instead of the use of NADH as an electron donor (Fig. 6). Enzymes can be immobilized on a suitable matrix to ensure stability and reusability. Xu et al. co-encapsulated three dehydrogenases in an alginate-silica (ALG-SiO_2) hybrid gel and reported a 98.1% CO_2-to-methanol conversion rate [199]. Addo et al. reported that a dehydrogenase enzyme cascade coupled with a poly(neutral red) modified electrode can regenerate NADH [200]. Schlager et al. (2016) developed a coenzyme-independent electrochemical system using dehydrogenases immobilized on carbon felt electrodes and directly injected electrons into the enzyme [106].

Similar to an electrochemical system, a photoelectric system can also be used for CO_2 reduction into a biofuel as solar energy can be used instead of an electric current for water splitting. Naturally, water and CO_2 are converted into life-supporting molecules by photosynthesis in the presence of solar energy. Mimicking this process by combining inorganic and organic processes together with water, CO_2 and light can be transformed into valuable compounds. During this process, solar energy drives production of the H_2 by splitting the H_2O using an inorganic catalyst. The produced H_2 is then used by microbial cells as a reducing equivalent for reduction of CO_2 to methane. Nichols et al. developed a bioinorganic hybrid system using platinum catalyst for water splitting and *Methanosarcina barkeri* as a biocatalyst for CO_2 capture and reported an 86% CO_2-to-CH_4 conversion [201]. However, such technologies are still in their initial stage and not applicable at an industrial level.

6.2. Integrated CO_2 capture and bioenergy production system

Different strategies can be utilized for conversion of CO_2 to bioenergy including, a) CO_2 capture from coal-fired plants using biological and other methods and use of it as feedstock for microbial fermentation (Fig. 7a), and b) CO_2 capture and use as feedstock for organic acid production and further converting these acids into bioenergy using microbial fermentation (two step system) (Fig. 7b), and c) simultaneous CO_2 capture and bioenergy production using a single-pot system (Fig. 7c). Lehtinen et al. developed a two-step bioprocess for conversion of CO_2 into alkane [202]. During the first step, *Acetbacterium woodii* captures CO_2 and produces acetic acid and during the second step

engineered *Acinetobacter baylyi* ADP1 utilizes the acetic acid and produces alkane. A similar type of process has been reported to produce other biochemicals from CO_2. Sciarria et al. used a microbial electrosynthesis system for volatile fatty acids (VFAs) from CO_2; the produced VFAs were extracted and further used as feedstock for a mixed culture fermentation to produce polyhydroxyalkanoates [203]. Use of an additional CO_2 capture process makes this production process costly. There is a need to develop an integrated single-pot system able to capture CO_2 and transform it into bioenergy while simultaneously avoiding an additional CO_2 transportation and storage step (Fig. 7c). This type of system can be developed by engineering CO_2-utilizing microbes with a bioenergy production pathway or engineering microbes that can produce bioenergy with a CO_2 capture pathway.

7. Conclusion

CO_2 capture and its conversion into energy is an interesting approach; however, it is still at its initial technological stage and currently has several drawbacks that make it more expensive or limit its practical application. The use of biological systems results in low productivity because of the requirement for cofactors and the sensitivity of microbes to high concentrations of CO_2. Thus, more robust enzymatic systems that can withstand harsh conditions (high temperatures, contaminants present in the flue gas, and ionic liquids) and regenerate various cofactors required to carry out the reactions are needed. Cooperation between international agencies, scientists, and industry is also needed. Government bodies should provide subsidies and frame policies to encourage industry to adapt CCS technologies. Industry and research institutes should join hands to redesign and integrate industrial plants for CO_2 capture and bioenergy production at the same site. Integration of the processes and the use of a hybrid system for CO_2 capture and bioenergy production together may help to overcome most of the challenges in this area (CO_2 storage and transportation) and improve the economics of the process.

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